Supplementary information

New Chiral ligands bearing two N-Heterocycle Carbene moieties at a Dioxolane backbone. Gold(I), palladium(II) and rhodium(I) complexes as enantioselective catalysts.

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Experimental Section

General Remarks: All preparations of metal complexes were carried out under dinitrogen by conventional Schlenk-tube techniques. Solvents were carefully degassed before use. C, H and N analysis were carried out by the analytical department of the Institute of organic chemistry (C.S.I.C.) with a Lecco apparatus. Metal contents were analyzed by atomic absorption using a Perkin Elmer AAnalyst 300 atomic absorption apparatus and plasma ICP Perkin Elmer OPTIMA 2100 DV. IR spectra were recorded on a Bruker IFS 66v/S spectrophotometer (range 4000-200 cm⁻¹) in KBr pellets. ¹H-NMR, ¹³C-NMR spectra were taken on Varian XR300 and Bruker 200 spectrometers. Chemical shifts being referred to tetramethylsilane (internal standard). Gas chromatography analysis was performed using a Hewlett-Packard 5890 II. The enantiomeric excess was measured by HPLC (Agilent 1200). AuCl(tht), ¹ PdCl₂(cod), [RhCl(cod)]₂,² [Rh(DIOP)(cod)]PF₆³ DIOP[AuCl]₂⁴were obtained as described in literature.

Synthesis of precursors.

3,3'-((4S,5S)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl)bis(methylene)bis(1-(2,4,6-

trimethylphenyl)-1H-imidazol-3-ium) iodide (S,S)[3a]I

A mixture of (4R,5R)-*bis*(iodomethyl)-2,2-dimethyl-1,3-dioxolane (2) (1.14 g, 3 mmol) and 1-(2,4,6-trimethylphenyl)-1*H*-imidazole (1a) (1.24 g, 6.6 mmol) was heated in acetonitrile at 140 °C for 48 h. The solvent was removed, the product washed with ethyl ether and filtered to afford the salt (2.07 g, 92%) as a white solid. IR (KBr; cm⁻¹): v= 3437 (C-N); 3049 (C-H); 2984-2928 (C-H); 1608 (C=C); 1560-1546 (C=N); 1445 (C-N); 1202-1163 (C-N). ¹H-RMN (CDCl₃) δ (ppm): 9.66 (2H, s, NCH=N); 8.29 (2H, s, CH_{im}); 7.24(2H, t, CH_{im}); 6.98 (4H, s, H_{arom}); 5.55 (2H, d, CH₂); 5.08 (2H, d, CH₂); 4.73(2H, d, OCH); 2.31 (6H, s, *p*-CH₃); 2.07 (12H, d, *o*-CH₃); 1.43 (6H, s, CH₃). ¹³C-

RMN (CDCl₃) δ (ppm): 141.36 (C(*p*-CH₃)); 137.42 (NCH=N); 134.06 (*C*(*o*-CH₃)); 134.29 (*C*(*o*-CH₃)); 130.38 (C_{arom}-N); 129.83 (CH_{arom}); 124.91 (CH_{im}); 122.89 (CH_{im}); 111.66 (C(CH₃)₂); 75.74 (OCH); 51.10 (CH₂); 27.43 (CH₃); 20.39 (*p*-CH₃); 17.63 (*o*-CH₃).

3,3'-((4*S*,5*S*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl)*bis*(methylene)*bis*(1-(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium) iodide (**S**,**S**)[**3**b]**I**

The procedure for [**3b**]**I** was followed using (4R,5R)-*bis*(iodomethyl)-2,2-dimethyl-1,3-dioxolane (**2**) (0.547 g, 1.433 mmol) and 1-(2,6-diisopropylphenyl)-1*H*-imidazolidine (**1b**) (0.72 g, 3.15 mmol). The product was purified by flash chromatography (acetone/ethyl acetate: 2/1) to give the salt (601 mg, 50%) as a light yellow solid. IR (KBr, cm⁻¹): v= 3436 (C-N); 3065 (C-H); 2964-2928 (C-H); 1625 (C=C); 1561-1541 (C=N); 1460 (C-N). ¹H-RMN (CDCl₃) δ (ppm): 9.77 (2H, s, NCH=N); 8.45 (2H, s, CH_{im}); 7.54 (2H, t, *p*-H_{arom}); 7.31-7.30 (4H, m, *m*-H_{arom}); 7.20 (2H, t, CH_{im}); 5.6 (2H, dd, CH₂); 5.25 (2H, dd, CH₂); 4.86 (2H, dd,OCH); 2.44-2.42 (2H, m, CH); 2.21-2.19(2H, m, CH); 1.26, 1.17, 1.16 (24H, d,d,d; CH₃-CH_{arom}); 1.43 (6H, s, CH₃). ¹³C-RMN (CDCl₃) δ (ppm): 145.43 (*o*-C_{arom}); 145.72 (*o*-C_{arom}); 137.90 (NCH=N); 132.32 (*p*-C_{arom}); 130.90 (C_{arom}-N); 125.29 (CH_{im}); 51.25 (CH₂); 28.93, 28.87 (CH); 27.78 (CH₃); 24.72, 24.70, 24.65, 24.26 (CH₃).

Synthesis of complexes.

General method: to a solution of [**3a**]**I** (1 mmol, 754 mg) or [**3b**]**I** (1 mmol, 838 mg) in dichloromethane, Ag₂O (1 mmol, 231 mg) was added and the mixture stirred at room temperature for 24 h under N₂ atmosphere. The mixture was filtered through Celite in order to remove unreacted Ag₂O and other insoluble solids. AuCl(tht) (2 mmol, 632 mg), PdCl₂(cod) (1 mmol, 259 mg) or [RhCl(cod)]₂ (0.5 mmol, 246 mg) was added to the solution of the resulting silver salt in CH₂Cl₂. After 3 h at room temperature, the mixture was filtered through Celite. The solvents were removed in vacuum, and the residue thoroughly washed with diethyl ether and/or pentane. Several attempts to obtain suitable crystals for X-ray diffraction were unsuccessful.

 $(S,S)[3a][Au(I)Cl]_2$ (**3aAu**): Pale yellow. Yield: 84%. M.p.: 138-141 °C. $C_{31}H_{38}N_4O_2Au_2Cl_2$ (963.5): C: 38.6; H: 4.0; N: 5.8; Au: 40.9; found C: 38.3; H: 4.1; N:

5.5; Au: 40.2 %. IR (KBr, cm⁻¹): v = 3142 (CH_{arom}); 1605 (C=C); 328 (Au-Cl). ¹H-NMR (CDCl₃, ppm): δ = 7.19 (2H, s, CH_{im}); 7.05-7.00 (4H, m, H_{arom}); 6.94 (2H, s, CH_{im}); 4.81-4.64 (2H, m, CH₂); 4.63-4.58 (2H, m, OCH); 4.53-4.39 (2H, m, CH₂); 2.32 (3H, s, *p*-CH₃); 2.30 (3H, s, *p*-CH₃); 2.00 (6H, s, *o*-CH₃); 1.97 (6H, s, *o*-CH₃); 1.45 (3H, s, CH₃); 1.35 (3H, s, CH₃). ¹³C-NMR (CDCl₃, ppm): δ = 177.12 (C-Au); 141.80 (C-N); 141.73 (C-N); 134.75 (C(*p*-CH₃)); 134.70 (C(*p*-CH₃)); 130.77 (CH_{arom}); 130.19 (CH_{arom}); 129.75 (C(*o*-CH₃)); 129.65 (C(*o*-CH₃)); 125.39 (CH_{im}); 124.69 (CH_{im}); 123.32 (CH_{im}); 123.10 (CH_{im}); 112.06 (C(CH₃)₂); 76.31 (OCH); 75.67 (OCH); 52.06 (CH₂); 51.20 (CH₂); 27.52 (CH₃); 27.19 (CH₃); 21.24 (*p*-CH₃); 17.92 (*o*-CH₃). ESI-MS (m/z): 927 (M⁺-Cl), 731 (M⁺-AuCl).

(S,S)[3b][Au(I)Cl]₂ (**3bAu**): Pale yellow. 85%. M.p.: 152-155 °C. C₃₇H₅₀N₄O₂Au₂Cl₂ (1046.6): C: 42.5; H: 4.7; N: 5.4; Au: 37.6; found C: 42.0; H: 4.6; N: 5.5; Au: 37.1 %. IR (KBr, cm⁻¹): v = 3140 (CH_{arom}); 1610 (C=C); 331 (Au-Cl). ¹H-NMR (CDCl₃, ppm): δ = 7.57 (2H, d, CH_{im}); 7.50-7.44 (3H, m, H_{arom}); 7.27-7.21 (3H, m, H_{arom}); 6.96 (2H, s, CH_{im}); 4.82-4.77 (2H, m, CH₂); 4.64-4.61 (2H, m, OCH); 4.53-4.43 (2H, m, CH₂); 2.54-2.48 (2H, m, CH), 2.31-2.23 (m, 2H, CH), 1.66-1.64 (6H, CH₃); 1.36-1.29 (12H, CH₃); 1.17-1.08 (12H, CH₃). ¹³C-NMR (CDCl₃, ppm): δ = 173.88 (C-Au); 146.40, 146.00 (C_{arom}-N); 134.33, 131.32 (*p*-CH_{arom}); 127.02 (*C*(*o*-CH₃)); 125.47 (*C*(*o*-CH₃)); 124.69 (CH_{im}); 123.32 (CH_{im}); 27.39 (CH₃); 24.77 (CH₃); ESI-MS (m/z): 1011 (M⁺- Cl), 815 (M⁺- AuCl).

 $(S,S)[3a][Au(OPNB)]_2$: A suspension of $(S,S)[3a][AuCl]_2$ (50 mg, 0.052 mmol) and AgOPNB (42 mg, 0.15 mmol, 3 equiv) in chloroform (1.5 mL) was sonicated for 5 min. The resulting off-white dispersion was filtered through a plug of celite (0.5 x 2 cm), washed with chloroform (3 x 2 mL), and concentrated to approximately 1 mL. A white solid formed upon dropwise addition of hexanes. The remaining solvent was removed *in vacuum* to afford (*S*,*S*) [**3a**][Au(I)(OPNB)]₂ as an analytically pure white solid. Yield: 61 %. M.p.: 148-150 °C. C₄₅H₄₆N₆O₁₀Au₂ (1224.8): C: 44.1; H: 3.8; N: 6.9; Au: 32.2; found C: 44.7; H: 4.1; N: 7.4; Au: 31.8 %. IR (KBr, cm⁻¹): v = 3153 (CH_{arom}); 1589 (C=O); 1522, 1333 (NO₂).¹H-RMN (CDCl₃, ppm): δ = 8.18-8.09 (8H, m, H_{OPNB}); 6.98-6.68 (8H, m, CH_{im}, H_{arom}); 4.76 (2H, m, CH₂); 4.55-4.46 (2H, m, CHO); 4.36-4.28 (2H,

m, CH₂); 2.43 (3H, s, *p*-CH₃); 2.40 (3H, s, *p*-CH₃); 1.99 (3H, s, *o*-CH₃); 1.81 (3H, s, *o*-CH₃); 1.70 (3H, s, *o*-CH₃); 1.54 (3H, s, *o*-CH₃); 1.40 (3H, s, OC(CH₃)₂); 1.27 (3H, s, OC(CH₃)₂). ¹³C-NMR (CDCl₃, ppm): δ = 185.76 (C-Au); 184.05 (C-Au); 169.00 (CNO₂); 149.08 (CNO₂); 141.37 (C-N); 139.78 (C-N); 134.80 (*C*(*p*-CH₃)); 134.50 (*C*(*p*-CH₃)); 130.53 (C_{OPNB}); 129.79 (CH_{arom}); 129.50, 129.00 (*C*(*o*-CH₃)); 124.88 (CH_{im}); 124.01 (CH_{im}); 122.86 (C_{OPNB}); 122.01 (CH_{im}); 111.41 (*C*(CH₃)₂); 76.04 (CHO); 75.31 (CHO); 54.49 (CH₂); 50.71 (CH₂); 29.67 (OC(*C*H₃)₂); 26.88 (OC(*C*H₃)₂); 21.03 (*p*-CH₃); 17.43 (*o*-CH₃). ESI-MS (m/z): 695 (3aAu).

(S,S)[3a][PdCl₂] (**3aPd**): Red-brown. Yield: 85 %. 188-190 °C. C₃₁H₃₈Cl₂N₄O₂Pd (676.0): C: 54.9; H: 5.9; N: 8.3; Pd: 15.7 % found C: 54.7; H: 5.6; N: 8.1, Pd: 15.1 %. IR (KBr, cm⁻¹): v = 1610 (C=C.); 1241, 1207 (C-O-C); 578 (Pd-C). ¹H-NMR (CDCl₃, ppm): $\delta = 7.10$ (2H, s, CH_{im}); 6.95 (4H, s, H_{arom}); 6.83 (2H, s, CH_{imi}); 6.23 (2H, d, J = 15 Hz, CH₂); 5.24-4.96 (2H, m, CH₂); 4.90-4.65 (2H, m, OCH); 2.36 (6H, s, *p*-CH₃); 2.10 (6H, s, *o*-CH₃); 2.04 (6H, s, *o*-CH₃); 1.61 (6H, s, (CH₃)₂C-). ¹³C-NMR (CDCl₃, ppm): $\delta = 175.00$ (C-Pd); 141.42 (C-N) 137.74 (*C*(*p*-CH₃)); 130.17 (CH_{arom}); 129.81 (*C*(*o*-CH₃)); 125.25 (CH_{imi}); 123.19 (CH_{im}); 112.14 (*C*(CH₃)₂); 77.79 (CHO); 52.82 (CH₂); 27.95 (OC(*C*H₃)₂); 21.49 (*p*-CH₃); 19.04 (*o*-CH₃). ESI-MS (m/z): 677 (M⁺), 605 (M⁺-2Cl).

(S,S)[3a][RhCl(cod)] (3aRh): Green-brown. Yield: 70 %. M.p.: 250 °C (dec.). C₃₉H₅₀ClN₄O₂Rh (745.2): C: 62.9; H: 6.8; N: 7.5; Rh: 13.6 % found C: 62.4; H: 7.3; N: 7.3; Rh: 13.0 %. IR (KBr, cm⁻¹): v= 1632 (C=C.); 1228, 1203 (C-O-C); 525 (Rh-C). ¹H-NMR (CDCl₃, ppm): δ = 7.09 (2H, s, CH_{im}); 6.99 (4H, s, H_{arom}); 6.88 (2H, s, CH_{im}); 6.18-6.02 (2H, m, CH₂); 5.20-5.00 (2H, m, CH₂); 4.97-4.54 (4H, m, OCH, CH_{cod}); 3.61-3.29 (2H, m, CH_{cod}); 2.56-2.18 (8H, m, CH_{2(cod)}); 2.40 (3H, s, *p*-CH₃); 2.30 (3H, s, *p*-CH₃); 2.06 (6H, s, *o*-CH₃); 1.97 (6H, s, *o*-CH₃); 1.60 (6H, m, (CH₃)₂C-). ¹³C-NMR (CDCl₃, ppm): δ = 179.81 (C-Rh); 141.23 (C-N) 132.20 (*C*(*p*-CH₃)); 130.17 (CH_{arom}); 129.06 (*C*(*o*-CH₃)); 126.33 (CH_{im}); 124.20 (CH_{imi}); 111.30 (*C*(CH₃)₂); 95.30 (CH_{(cod})); 78.46 (CHO); 69.33 (CH_{(cod})); 53.41 (CH₂); 28.42 (CH_{2(cod})); 27.72 (OC(*C*H₃)₂); 21.39 (*p*-CH₃); 18.29 (*o*-CH₃). ESI-MS (m/z): 745 (M⁺). **NHC cationic complexes** were generated by halide abstraction via addition of AgPF₆ in a CH₂Cl₂/water solvent system. The ¹H- and ¹³C-NMR spectra were found to be very similar to those of neutral complexes and do not provide direct evidence for the generation of the cationic complexes, the generation of which is established by their analytical data. The infrared spectra display a vibrational band at 850 cm⁻¹ which is assigned to v(P-F) stretching mode.

(R,R)-DIOP[AuN(SO₂CF₃)₂]₂: To a solution of (R,R)-DIOP[AuCl]₂ (50 mg, 0.52 mmol) in CH₂Cl₂ was added silver bis(trifluromethanesulfonyl)imide (40.3 mg, 1.04 mmol). The resulting off-white dispersion was filtered through a plug of celite and the solvent evaporated. (R,R)-DIOP[AuN(SO₂CF₃)₂]₂ was obtained as a white solid in quantitative yield.

 $\{(R,R)\text{-DIOP}[Au(PhCN)]_2\}PF_6$: To a solution of $(R,R)\text{-DIOP}[AuCl]_2$ (50 mg, 0.52 mmol) in benzonitrile was added AgPF₆ (26.2 mg, 1.04 mmol). The mixture was filtered through a plug of celite and the solvent evaporated. $\{(R,R)\text{-DIOP}[Au(PhCN)]_2\}PF_6$ was obtained as a white solid in quantitative yield.

Hydrogenation of alkenes

The catalytic properties, in hydrogenation reactions, of the complexes were examined under conventional conditions for batch reactions in a reactor (Autoclave Engineers) of 100 mL capacity at 40 °C temperature, 4 atm. dihydrogen pressure and 1/1000 metal/substrate molar ratio. The evolution of the reaction of hydrogenated product was monitored by gas-chromatography. The enantiomeric excess was measured by HPLC using chiral column chiralcel OD [diethyl 2-benzylidene succinate, λ : 250 nm, Hexane/iPrOH: 95/5, 0.5 mL/min flow rate, chiralcel AD-H [diethyl itaconate, λ : 230 nm, Hexane/ⁱPrOH: 98/2, 0.4 mL/min flow rate. The absolute configuration was determined by correlation with the literature [5]. An example was shown in figure S1



Figure S1. HPLC traces for diethyl 2-benzylsuccinate: racemic from Pd/C (top image), hydrogenated product from **3aAu** (bottom image).

Variation of catalyst activity with time



Figure S2. Deviation of catalytic activity with time.

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